

The effects of ac potentials on the crystallography of noble metals

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The surface of a solid is the intrinsic defect of a crystal. As a consequence, surface atoms tend to minimize their free energy by lateral displacements to more stable positions. It was found that the application of low-frequency-ac potentials to noble metals produce a redistribution of crystallographic planes. These effects disappear after a few cycles in the oxide region. Two ac potentials were used;

Program 1):  $\phi_1 = 0.05\text{ V}$ ,  $\phi_2 = 0.50\text{ V}$ ,  $\nu = 10\text{ Hz}$

Program 2):  $\phi_1 = 0.65\text{ V}$ ,  $\phi_2 = 1.50\text{ V}$ ,  $\nu = 25\text{ Hz}$

An original polycrystalline (pc) platinum surface shows XRD patterns with a great contribution of the (220) plane (78 % integrated signal) and the (311) plane (8 %). When Program 1) is applied to pc platinum, XRD patterns exhibit a larger contribution of (200) planes (Fig.1). On the other hand, the application of Program 2) produces an increase of (111) planes (Fig. 2).

Platinum-atom-displacements in the lattice can be calculated from the expression of the dynamical matrix modified with the ac potential.

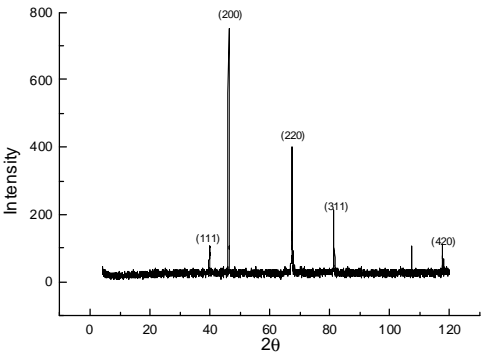
$$M\omega^2\epsilon_j = \mathbf{D}(\mathbf{k})\epsilon_j + (e\phi_i/r) \cdot \epsilon_j \quad (1)$$

Being  $\epsilon_j$  the components of the polarization vector with  $\mathbf{k}$  of the first Brillouin zone,  $\omega$  the vibration frequency,  $\mathbf{D}(\mathbf{k})$  the dynamical matrix of the interionic forces, and  $\phi_i(t)$  the ac potential.

There are two solutions for the motion eq. (1), which are evaluated within the two halfperiods of the ac potential. In both cases, the original planar waves that describe the vibration of platinum atoms in the lattice are reduced to single longitudinal vibrations during the application of the Program. As a consequence, a linear atomic displacement occurs, which destroys the original crystalline orientation. This effect results in a new crystallography. The new equilibrium position,  $r'$ , can be obtained from the potential energy and its derivation with respect to  $r'$ ,

$$r' = r \sqrt{\frac{\phi_2}{\phi_1}} \text{ with } \phi_2 > \phi_1 \quad (2)$$

Figure 1.- XRD patterns of a platinum plate treated with Program 1. The X-ray diffractions were obtained with a step size of  $0.02^\circ$  and 0.5 s of time per step



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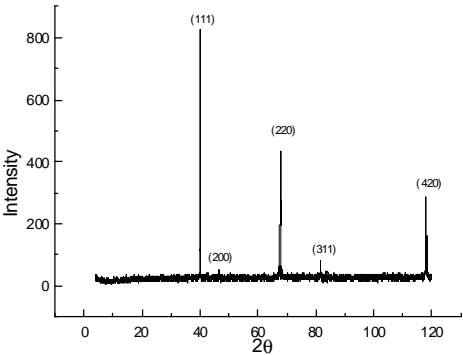


Figure 2.- XRD patterns of a platinum plate treated with Program 2.